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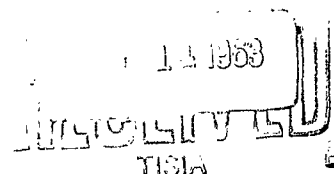**ARLINGTON 12, VIRGINIA**

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Collisional Transition Probabilities for Vibrational Deactivation of Chemically Activated sec-Butyl Radicals.   Diatomic and Polyatomic Molecules. [*]

by

G. H. Kohlmaier and B. S. Rabinovitch

Department of Chemistry, University of Washington

Seattle

Abstract

The study of collisional transitional probabilities for the de-excitation by inert gases of chemically activated sec-butyl radicals, excited to internal energies in excess of 40 kcal mole^{-1}, has been extended to H_2, D_2, N_2, CO_2, CH_4, CD_3F, CH_3Cl and SF_6. The diatomic gases display behavior similar to the rare gases, and on a preferred exponential model of collisional transition probabilities the average amount of energy transferred per collision is $\langle \Delta E \rangle_{expon} \cong 1.3$ kcal mole^{-1}. On a step-ladder model the corresponding amount is $\Delta E \cong 2.5$ kcal mole^{-1}. From higher pressure data, the efficiency (assumed ΔE) for CD_3F, CH_3Cl and SF_6 is deduced to be comparable with that for butene and on a preferred step-ladder model, $\Delta E > 9$ kcal. For CO_2 and CH_4 the behavior is intermediate. The possible importance of the role of internal rotation of butyl in facilitating energy transfer is noted; some uncertainty concerning the role of overall rotations and vibrational modes of the deactivator in the relaxation process exists.

INTRODUCTION

Earlier papers in this series have described the behavior of butene[1] and of the rare gases[2] as collisional deactivating agents for vibrationally excited sec-butyl radicals. The latter were produced by chemical activation.[3] Non-equilibrium distributions were obtained at vibrational levels of the ground electronic state grouped above 40 kcal mole^{-1}; the radicals could decompose at energy E > 33 kcal mole^{-1}, the critical energy. Collisional degredation below this threshold resulted in stabilization.

Butene was found to remove energy with a collisional transition probability which was distinctly higher for large energy jumps (many kilocalories) than for small ones (a few calories). A step-ladder probability scheme is a useful descriptive model and $\Delta E \geqslant$ 9 kcal mole^{-1}.

The rare gases He, Ne, Ar, Kr on the other hand were characterized on a step-ladder model by values which increased with atomic weight in the range 2.5 - 3.5 kcal mole^{-1}. However, an "exponential" model (actually any model in which very small jumps are more probable than larger ones) seems to be a better description. Although subject to the uncertainties of the details of the model which the data were not sufficiently precise to discern, the results are usefully described on this basis as giving $\langle \Delta E \rangle$ = 1.0 - 1.7 kcal mole^{-1} for these gases.

In order to explore the effects of varying molecular structure and isotopic substitution, these studies have been extended to other inert deactivating gas: the use of the diatomic molecules H_2, D_2 and N_2, the triatomic CO_2 and polyatomic gases, CH_4, CH_3Cl, CD_3F and SF_6 is reported here. Valuable information on inert gases of

varying structure and complexity as deactivators of β-napthylamine and other emitters, at vibrational levels somewhat below these, has been reported by several groups.[4-7]

EXPERIMENTAL

Materials and Apparatus

The cis-butene-2 purity was described previously. CH_3Cl and SF_6 were Matheson commercial grade and were purified by (GLPC) to 99.8% purity. A sample of CD_3F was generously donated by Dr. D. F. Eggers, and was similarly checked by gas-liquid phase chromatography, GLPC . The chemical impurities (< 1%) were non-interfering substances (CH_4 and higher products also). CH_4 was Phillips research grade of purity 99.6% and was checked by GLPC. CO_2, H_2 and N_2 were Air Reduction Company assayed reagent grade (> 99.99%) and were not further treated. D_2 was obtained from General Dynamics and was of 99.5% purity. H_2, D_2 and N_2 were deoxygenated over hot tungsten by heating, as described previously for the rare gases. Since the experiments were carried to low pressures (low percentage stabilization) only for the diatomic gases, possible oxygen impurity effects described in II were not important for the more complex gases.

Other aspects of the technique were similar to that described previously.[3,8]

Procedure and Analysis

This also followed the earlier work. The percent reaction of butene substrate was kept around 5%, and under 10%. The low

boiling inert gases, H_2, D_2, N_2 and, in part, CH_4, were separated from the products by freezing with liquid or solid N_2 and pumping. CO_2 was removed by absorption on ascarite. Other inert gases, where they interfered, were first separated from the products by GLPC to a sufficient degree so that analysis of the mixtures could proceed.

RESULTS

Corrections to the data are similar to those described earlier in II.

Values of the measured apparent average rate constants,[3] k_a = ω D/S, were calculated on the basis of hard-sphere collision cross-section σ^2 (Appendix I). Conversion factors for k_a, based on other more appropriate collision cross-sections, are also given in Appendix I. Rate data for the gas mixtures at 300° K are summarized in Figures 1 and 2. Figure 1 presents k_a as a function of S/D for mixtures of butene with the other inert gases used. The nature of the technique is such that the inert gas butene, which is the progenitor of the sec-butyl radical, is inevitably present in some amount in the system. The diatomic molecule mixtures were cis-butene-2:H_2 (1:14 p, 1:27 c); cis-butene-2:D_2 (1:14 p, 1:20 c) and cis-butene-2:N_2 (1:29 p, 1:21 c); and pure cis-butene-2. The symbol p stands for relative pressures, and c for relative collision numbers on the hard-sphere basis. In Figure 2 are given similar data for triatomic and polyatomic inert deactivators, cis-butene-2: CO_2 (1:30 p, 1:21 c), cis-butene-2:CH_4 (1:24 p, 1:23 c), cis-butene-2: SF_6 (1:22 p, 1:15 c), cis-butene-2:CD_3F (1:27 p, 1:20 c), and cis-butene-2:CH_3Cl (1:20 p, 1:14 c) and pure cis-butene-2. The polyatomic inert gases were investigated only in the higher pressure

region; their high efficiency, relative to butene, early indi-
cated that "turn-up" would scarcely be detectible unless the data
were pushed far into the lower pressure region where accuracy suf-
ficient to reward the effort required was not available. Similar
presentations of the data for the diatomic gas mixtures, of the
same dilutions as at 300°, are given in Figures 3 and 4 for 195°
and 373° K. The polyatomic gas mixtures were not studied at these
temperatures.

The figures show that, on the hard-sphere basis employed, k_a
increases at all temperatures in the order, pure butene, N_2, D_2
and H_2, with D_2 and H_2 being about the same at 195°. The rate con-
stants for the polyatomic gases at 300° are larger for CH_4 and CO_2
than for butene, and for SF_6, CH_3Cl and CD_3F are equal to or slightly
smaller than that for butene.

At 300° and 373°, the lower pressure (lower S/D) measurements
for the diatomic gas mixtures gave turn-up which started at approxi-
mately the same S/D region as found for the rare gas data of Part
II. No attempt will be made to evaluate the data at 373° quanti-
tatively, both because of the sparcity of the data and especially
because of increased occurrence of secondary and side-reactions.

ANALYSIS OF THE DATA

As in II, the analysis of the data is made in two parts: com-
parison of the magnitude of the observed rate constants with calcu-
lated values in the quasi-constant higher pressure region; and ex-
amination of the turn-up of the apparent rate constant in the lower
pressure region -- for example, by comparison of the function

k_a/k_{amin} with the calculated function $k(s)/k(s)_{min}$.

Higher Pressure Region

Two limiting interpretations from the higher pressure region are given:

Case I: ΔE_A assumed > 10 kcal,

$$k_{aAB}/k_{aA} = (1 - \alpha) + \alpha\beta_{min} \tag{II-27}$$

where β_{min} is an "all-or-nothing" efficiency factor for the inert gas A relative to butene B, and $(1 - \alpha)$ is the collisional dilution of the mixture A:B.

Case II: β_{min} is assumed unity, $\Delta E_A = \Delta E_{min}$; where ΔE_{min} is the minimum amount of energy transferred on a collision. This condition corresponds to an earlier stipulation of Bowen and Veljkowic[7].

It should be noted that ΔE for butene is > 9 - 10 kcal, in any case.

$\underline{\beta_{min}}$. Dependence on σ^2

Average values of β_{min} were obtained over a range of S/D of 0.5 - 1.5 at 195°, 0.3 - 0.8 at 300°, and 0.1 - 0.2 at 373° K. The β_{min} values for each rare gas, and their dependence on the assumed cross-sections, are given in Table I. β_{minh} and β_{minL-J} refer to values obtained from the hard-sphere and Lennard-Jones cross-sections, respectively (Appendix I). Two less-likely models for collision cross-sections, which were designated as σ_a^2 and σ_r^2 in II, are omitted here but are treated elsewhere.[8] Both β_{minh} and β_{minL-J} increase generally with increase of molecular weight and complexity of the inert gas, except that β_{minh} for H_2 and D_2 are approximately

the same at 195° K; this is subject to error because of the limited number of runs for D_2, but the difference between H_2 and D_2 is not marked in any case. Table I reveals the relative invariance of β_{min} with cross-section for the heavier gases. The large efficiencies of all polyatomic gases is noteworthy; some magnitudes are slightly in excess of unity, but are subject both to possible error in assumed cross-sections, and to experimental error.

ΔE_{min}. Dependence on σ^2

The quantity k_{aAB}/k_{aB} is compared with the results from a step-ladder calculation $k(s)/k(10)$, given previously in Part II, Figure 10. The results are summarized in Table II in terms of ΔE_{minh} and ΔE_{minL-J}.

For $\Delta E_{min} > 5$ kcal, the step values are only rough estimates since differences in $k(s)$ become progressively smaller, while the accuracy of the data remains constant. For the heavier complex molecules, ΔE_{min} becomes large and equal in order of magnitude to the value for butene. Methane and carbonddioxide are estimated to transfer on the average at least half the energy characteristic of butene. The ΔE_{min} values, analogous to the β_{min} quantities, decrease most markedly for the light diatomic gases, and are similar in magnitude to values found for the gases He and Ne.

Lower Pressure Region

Step-Ladder Model

Lower pressure "turn-up" functions of the form described in Part II, $c_a k_n/k_{amin}$ vs S/D (Figure 5), were obtained for the gases H_2, D_2 and N_2 at 300° K. Comparison with the function $c_a k(s)/k(s)_{min}$,

graphed previously in II, Figure 4, yields the average amount of energy, ΔE, transferred per collision on a step-ladder model. ΔE is 2.5 kcal mole^{-1} for all the diatomics H_2, D_2 and N_2; these values are quite similar to those for He and particularly Ne; N_2 might have been expected to be characterized by a larger value than for H_2 -- and this is quite possibly so, but the data for N_2 are limited.

These ΔE values for H_2 and D_2 do not entirely explain the magnitude of their high pressure constants; an efficiency factor of 0.57 similar to those for the rare gases (0.64), must be invoked. For N_2 such a factor is not necessary, i.e. unity.

Exponential Model

For an exponential model of collisional transition probabilities, described as $p_{ij} = ae^{-a(j-i)}$, the turn-up corresponds to $\langle \Delta E \rangle$ 1.3 kcal mole^{-1} for all gases. The exponential model for H_2 and D_2 gives more satisfactory agreement of the higher pressure rate constants with the lower pressure turn-up. For N_2, from the last sentence of the preceding section the contrary is evidently true. This is the only exception found for these atoms and smaller molecules to the general consensus in favor of the exponential model, and it is surmised that the exception is only apparent.

DISCUSSION

Rotational Transitions

Stevens[6] has presented a model of a collisional complex in terms of the formation of transitional oscillators. Linear and angular momentum conservation restrict redistribution of internal energy between collision partners. A simple case is an atom A with particle B, both of which have no intrinsic angular momentum, but where B is defined to have internal energy. For an inelastic collision,[9]

$$\frac{1}{2}\mu\dot{r}_1^2 + \frac{1}{2}\mu\frac{b_1^2 g_1^2}{r^2} + V(r) + \Delta E = \frac{1}{2}\mu\dot{r}_2^2 + \frac{1}{2}\mu\frac{b_2^2 g_2^2}{r^2} + V(r) \quad .$$

Subscripts 1 and 2 designate the conditions "before and after"; ΔE is the change in internal energy of B; g is the total relative velocity at infinite separation; $\dot{r}$ is the relative radial velocity; μ is the reduced mass; and b is the impact parameter, defined as the distance of closest approach in the absence of a potential $V(r)$. For conservation of angular momentum, $b_1 g_1 = b_2 g_2$, and $\frac{1}{2}\mu\dot{r}_1^2 + \Delta E = \frac{1}{2}\mu\dot{r}_2^2$, so that internal energy is exchanged with motion along the line of centers.

If B may have intrinsic angular momentum then a change of the system angular momentum L_{AB} due to the relative motion of the particles is allowed, providing that the total $L = L_{AB} + L_B$ is conserved. Thus for a butyl radical - atom collision, internal energy may be transferred into rotational energy of the two particle system and of butyl itself. This corresponds to the three transitional modes of Stevens for this case. For a butyl radical - diatomic

molecule collision, five transitional modes arise; while for a
butyl radical - polyatomic molecule collision, six transitional
modes may be active.

On this basis, an appreciable increase in efficiency (i.e. of
ΔE), for H_2, D_2 and N_2, relative to the atomic deactivators, may
be expected due to the two additional rotational degrees of freedom
(i.e. two more transitional modes). Values of β_{min} and of ΔE_{min}
(Table II) for H_2, D_2 and N_2 are only slightly larger, if at all, for the for-
mer two than those of the rare gases of similar molecular weight. ΔE values are known less accu-
rately and therefore will not be used in this relative comparison.

The relative values of H_2, D_2 and He are in accord with those
of Stevens, and Boudart and Dubois, for the β-napthylamine fluores-
cence system, but differ from those of Neporent and Mirumyants, for
the 3-dimethylamino-6-aminophthalimide system, where D_2 was found
to be appreciably more efficient than H_2 and He. For our system,
we conclude that vibrational - rotational transfer may be important
for N_2 (cf. ref 4) but no gross effects seem to be operative for
H_2 and D_2, relative to He. No gross mass effect exists for H_2 rela-
tive to D_2; the latter is slightly more efficient. By contrast,
important rotational effects opposite in direction, on replacement
of H by D have been found in the low energy region for species such
as CH_4, CD_4,[10] and H_2O, D_2O.[11]

The absolute values of ΔE for H_2, D_2 (like He) in the butyl
system are many-fold higher than those found from the fluorescence
studies.[4-6] Part of the difference can be accounted for by the
higher energy states and smaller excited molecule under considera-
tion here; part of the discrepancy may be resolved by the different
fluorescence data analysis, in which both a $\beta = 1$ and a hard-sphere

cross-section assumptions seem to enter; (the hard-sphere efficiency of N_2 is appreciably higher here, also, than on other bases). Some other reasons for such a difference were considered previously. In addition, however, there exists another mechanism for energy transfer which may be of greater importance for the present system, which is now considered.

Under collisional perturbation, some energy of the several internal rotations of butyl may be converted into overall rotational energy of the butyl radical (as well as system rotation), without change of net angular momentum. Such energy transfer from active internal rotational modes reduces the rate constant, k_E. This may be expected to be a facile mode of energy transfer here. For one NH_2 substituent on the massive β-napthylamine frame, the momentum conservation restriction would not be greatly relaxed and this mechanism should not operate effectively. This model may be tested by restricting internal rotation with use of alkyl radical such as cyclopentyl.

Vibrational Transitions

Stevens[6] suggested that transitional modes equilibrate with vibrational degrees of freedom of the excited species faster than do internal vibrational modes of the deactivator. The vibrational frequencies for H_2, D_2 and N_2 lie so high that, even on the assumption of complete equilibration of an intermediate collision complex, scarcely any effect due to this vibrational degree of freedom could be expected. The large value, $\Delta E \geqslant 9$ kcal, found for butene and similar large values for SF_6, CD_3F and CH_3Cl, as derived from the comparative efficiencies, suggest that vibrational - vibrational transfer is important for complex polyatomic molecules. Under the

exclusion of net vibrational - vibrational transfer the maximum average energy transferred from butyl would be $\langle\Delta E\rangle_{max}$ = 8.3 kcal (for 25 equivalent classical oscillators in the butyl radical at the energy involved), from the relation $\langle\Delta E\rangle$ = $(6/(25 + 6))$ 43 kcal. (Our data provides no criteria for distinction between polar and non-polar deactivators.)

Stevens[6] suggested that internal modes played a role only for higher alkanes, pentane and hexane, and not for smaller ones in his system of alkane deactivating gases. Our results for CO_2 and particularly CH_4 could satisfy a condition of no vibrational-vibrational energy transfer if rotational degrees of freedom were efficient sinks. However it seems unclear that rotations could be so effective for a molecule such as CH_4, when they have a lesser effect for N_2, which has larger moments of inertia.

We believe it probable that, apart from diatomic molecules with high frequencies, vibrational - vibrational transfer is significant even for the smaller polyatomics. Absolute values of ΔE for more complex molecules are in reasonable agreement with the fluorescence studies[6] of β-napthylamine, where energies transferred reach 5 kcal for complex deactivators at excess vibrational energies of the excited molecule in excess of 24 kcal.

A number of aspects of this phenomenon await experimental clarification — particularly the role played by overall rotations, especially as between diatomic and polyatomic deactivators, and by internal vibrational degrees of freedom of the energy sink.

Appendix I

Collision Cross-Sections

A detailed discussion has been given previously in Part II, Appendix II. $\sigma^{(h)}$ and ε/k given in Table II are the conventional 6,12 Lennard-Jones parameters. For the hard-sphere potential σ was set equal to $\sigma^{(h)}$. For the Lennard-Jones potential σ was evaluated using the Ω integral (see II) and called σ^{L-J}.

Collision radii for sec-butyl - inert gas relative to sec-butyl - cis-butene-2 are listed in Table III for the two potential models ($\sigma^{(h)}_{A,Bu}$ and $\sigma^{L-J}_{A,Bu}$).

Footnotes

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1. R. E. Harrington, B. S. Rabinovitch and M. R. Hoare, J. Chem. Phys. 33, 744 (1960).

2. G. H. Kohlmaier and B. S. Rabinovitch, J. Chem. Phys. , (1963); called II, hereafter.

3. B. S. Rabinovitch and R. W. Diesen, J. Chem. Phys. 30, 735 (1959); R. F. Kubin, B. S. Rabinovitch and R. E. Harrington, J. Chem. Phys. 37, 937 (1962).

4. B. S. Neporent and S. O. Mirumyants, Opt. and Spect. 8, 336 (1960); ibid, 8, 414 (1960).

5. M. Boudart and J. T. Dubois, J. Chem. Phys. 23, 223 (1955); B. Stevens and M. Boudart, Annals New York Acad. Sciences 67, 571 (1957).

6. B. Stevens, Mol. Phys. 3, 589 (1960).

7. E. J. Bowen and S. Veljković, Proc. Roy. Soc. (London) A236, 1 (1956).

8. G. H. Kohlmaier, Ph.D. Thesis, University of Washington, 1962.

9. F. O. Hirschfelder, C. F. Curtiss and R. B. Bird, Molecular Theory of Gases and Liquids, New York: J. Wiley and Sons, Inc., 1954.

10. T. L. Cottrell and A. J. Matheson, Proc. Chem. Soc. (London) 17 (1962).

11. J. C. McCoubrey, R. C. Milward, and A. R. Ubbelohde, Proc. Roy. Soc. A269, 156 (1962).

12. H. W. Melville and J. C. Robb, Proc. Roy. Soc. A202, 181 (1950).

Table I

β_minh and β_minL-J at 195°, 300° and 373° K for All Gases

Mixture (c)	195°		300°		373°[a]	
	β_{minh}	β_{minL-J}	β_{minh}	β_{minL-J}	β_{minh}	β_{minL-J}
He[b] 1:23	0.30	0.55	0.17	0.35	0.14-0.18	0.25-0.31
H₂ 1:27	0.31	0.48	0.21	0.30	0.13-0.17	0.18-0.24
D₂ 1:20	0.30	0.48	0.25	0.35	0.18-0.22	0.24-0.30
N₂ 1:21	0.60	0.67	0.47	0.54	0.28-0.34	0.31-0.37
CO₂ 1:21			0.75	0.83		
CH₄ 1:23			0.78	0.73		
CD₃F 1:20			1.12	---c		
CH₃Cl 1:13			1.13	0.82		
SF₆ 1:15			1.06	1.00		

(a) Uncertainty spread due primarily to side and secondary chemical reactions.

(b) Data of Part II.

(c) σ^2_{L-J} not available.

Table II

Step-Ladder Values (kcal mole^{-1}) of ΔE_{minh} and ΔE_{minL-J} at 195°, 300° and 373° K

Mixture (a)	195°		300°		373°[a]	
	ΔE_{minh}	ΔE_{minL-J}	ΔE_{minh}	ΔE_{minL-J}	ΔE_{minh}	ΔE_{minL-J}
H$_2$ 1:27	1.0	1.5	0.8	1.7	0.7-1.0	1.0-1.4
D$_2$ 1:20	1.0	1.5	1.0	1.7	1.0-1.6	1.5-1.8
N$_2$ 1:21	2.1	2.7	2.3	2.6	1.5-2.1	1.7-2.2
CO$_2$ 1:21			~4	~4		
CH$_4$ 1:23			~4	~5		
CD$_3$F 1:20			≳9			
CH$_3$Cl 1:14			≳9	≳7		
SF$_6$ 1:15			≳9	≳9		

(a) See Table I.

Table III

Collision Cross-Section Parameters

	ε/k cal.	$\sigma^{(h)}$ Å	$\sigma_{A,Bu}^{(h)}$ (rel.)		$\sigma_{A,Bu}^{L-J}$ (rel.)		
					195°K	300°K	373°K
H_2	66	2.97[a]	0.78	0.73	0.59	0.61	0.63
D_2	78	2.95[a]	0.78	0.73	0.60	0.62	0.63
N_2	182	3.68[a]	0.85	0.79	0.72	0.73	0.74
CO_2	377	4.00[a]	0.88	0.81		0.77	
CH_4	272	3.88[a]	0.86	0.80		0.82	
SF_6	399	5.51[a]	1.02	0.92		0.96	
CH_3Cl	1700	3.38[a]	0.82	0.76		0.93	
CD_3F	---	4.0[c]	0.88	0.81		---	
C_4H_8	620	5.3[a] 6.5[b]	1.00[a]	1.00[b]	1.00	1.00	1.00
C_4H_9	800[c]	(5.3 6.5)					

a) $\sigma^{(h)}$ values obtained from ref. (ℓ_1^{J}), except C_4H_8 which was assigned by comparison with a listed value for C_4H_{10}, as guided by the relation between values for C_2H_4 and C_2H_6

b) $\sigma^{(h)}$ values used by Melville and Robb[12], and in previous studies

c) estimated value

Figure 1: k_a vs S/D for the gases H_2, D_2, N_2 and cis-butene-2 at 300°K. → 0 are points outside the chosen scale. The curves in the Figures 1-4 were drawn in so as to pass through such points when extended beyond the scale. ○ ,H_2 1:27c; ● ,D_2 1:20c; □ N_2 1:21c; △, cis-butene-2.

Figure 2: k_a vs S/D for the gases CO_2, CH_4, SF_6, CD_3F, CH_3Cl and cis-butene-2 at 300°K. ○ , CO_2 1:30c; ● ,CH_4 1:24c; ▉ ,SF_6 1:22c; ◗ , CD_3F 1:20c; □ CH_3Cl 1:14c; △ , cis-butene-2.

Figure 3: k_a vs S/D for the gases H_2, D_2, N_2 and cis-butene-2 at 195°K. ○ , H_2 1:27c; ● ,D_2 1:20c; □ ,N_2 1:21c; △ , cis-butene-2.

Figure 4: k_a vs S/D for the gases H_2, D_2, N_2 and cis-butene-2 at 373°K. ○ , H_2 1:27c; ● , D_2 1:20c; □ , N_2 1:21c; △ , cis-butene-2.

Figure 5: Plot of corrected experimental curves of k_a/k_{amin} vs S/D. Experimental points left off for clarity. 1 = N_2 1:21c, 2 = D_2 1:20c, 3 = H_2 1:27c.
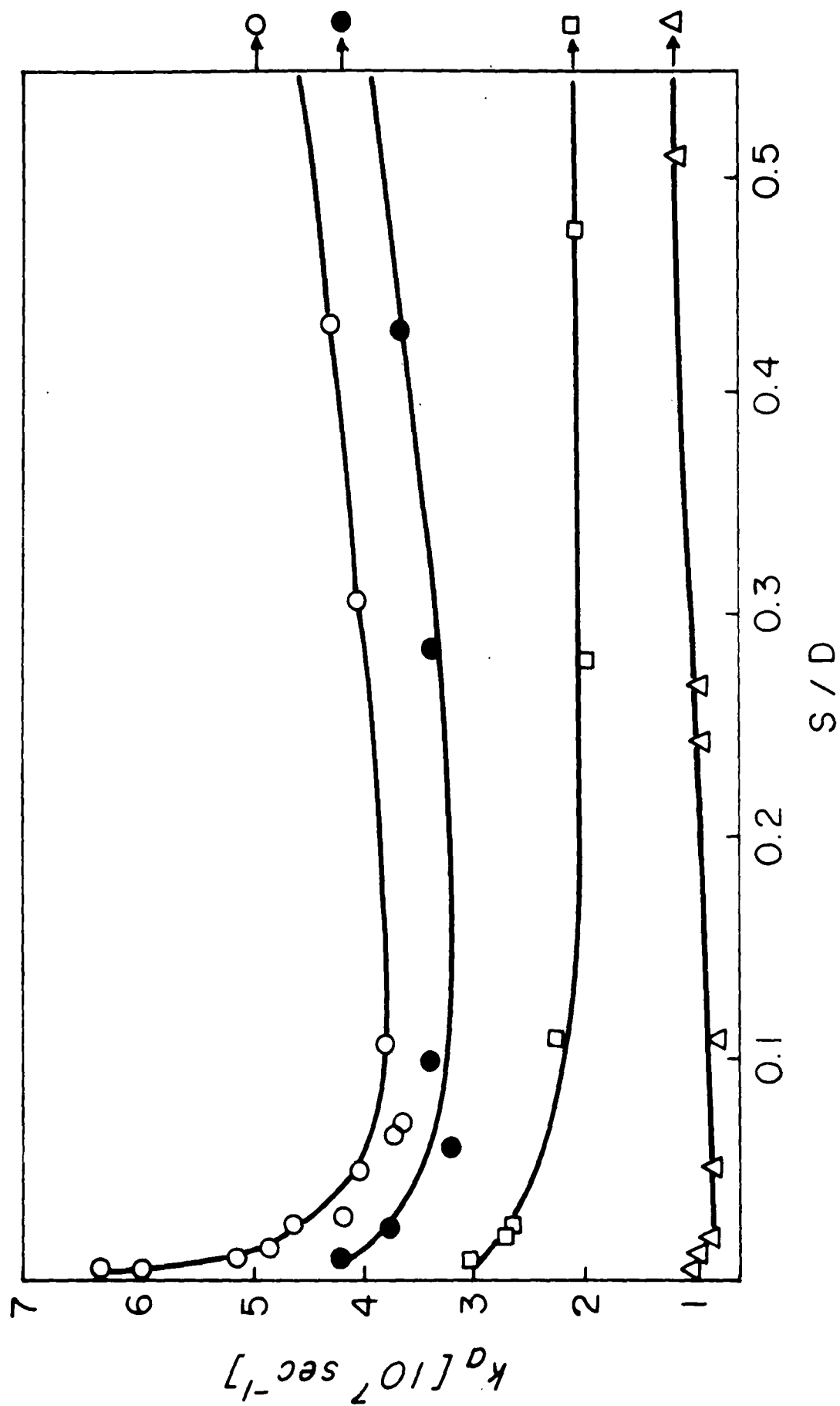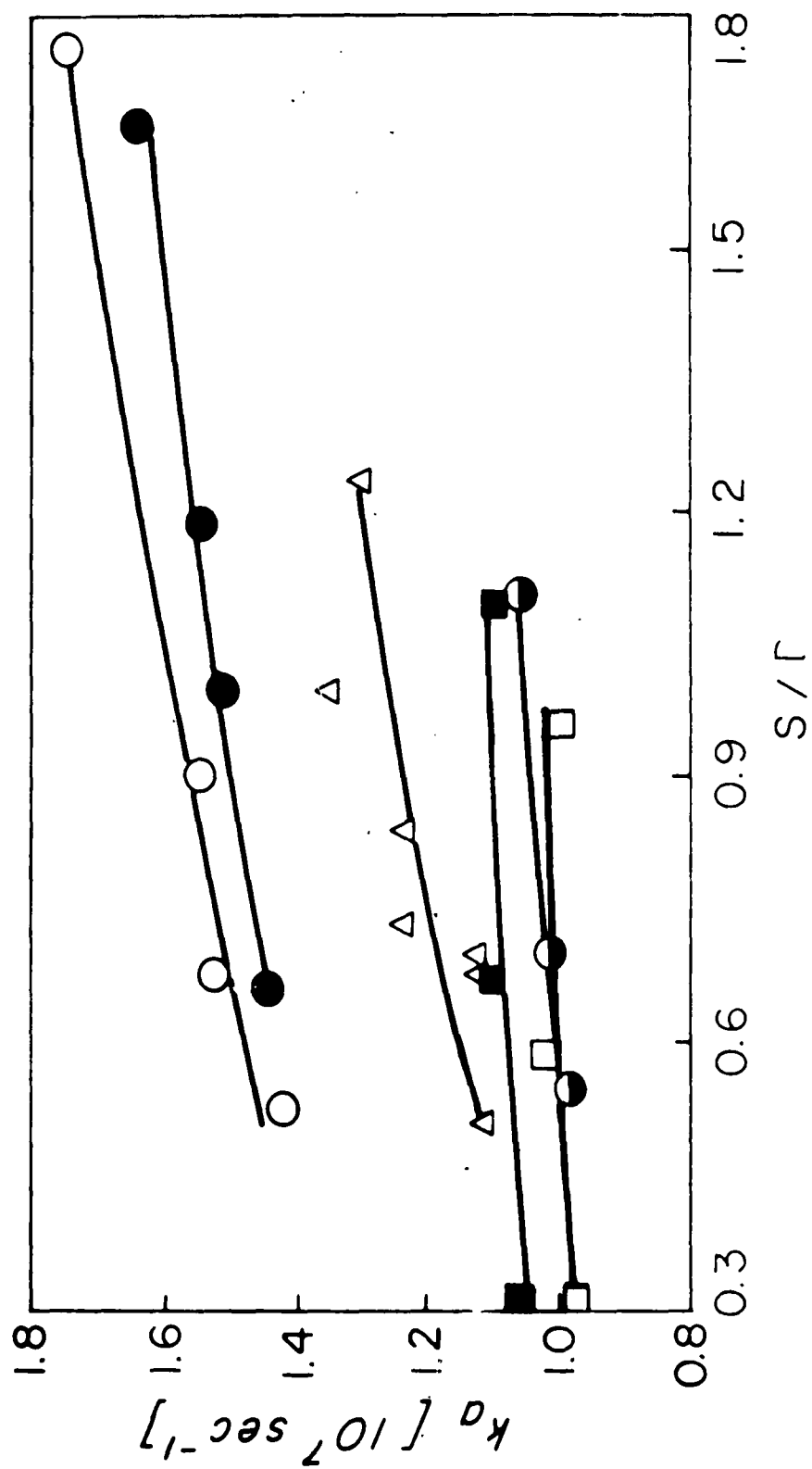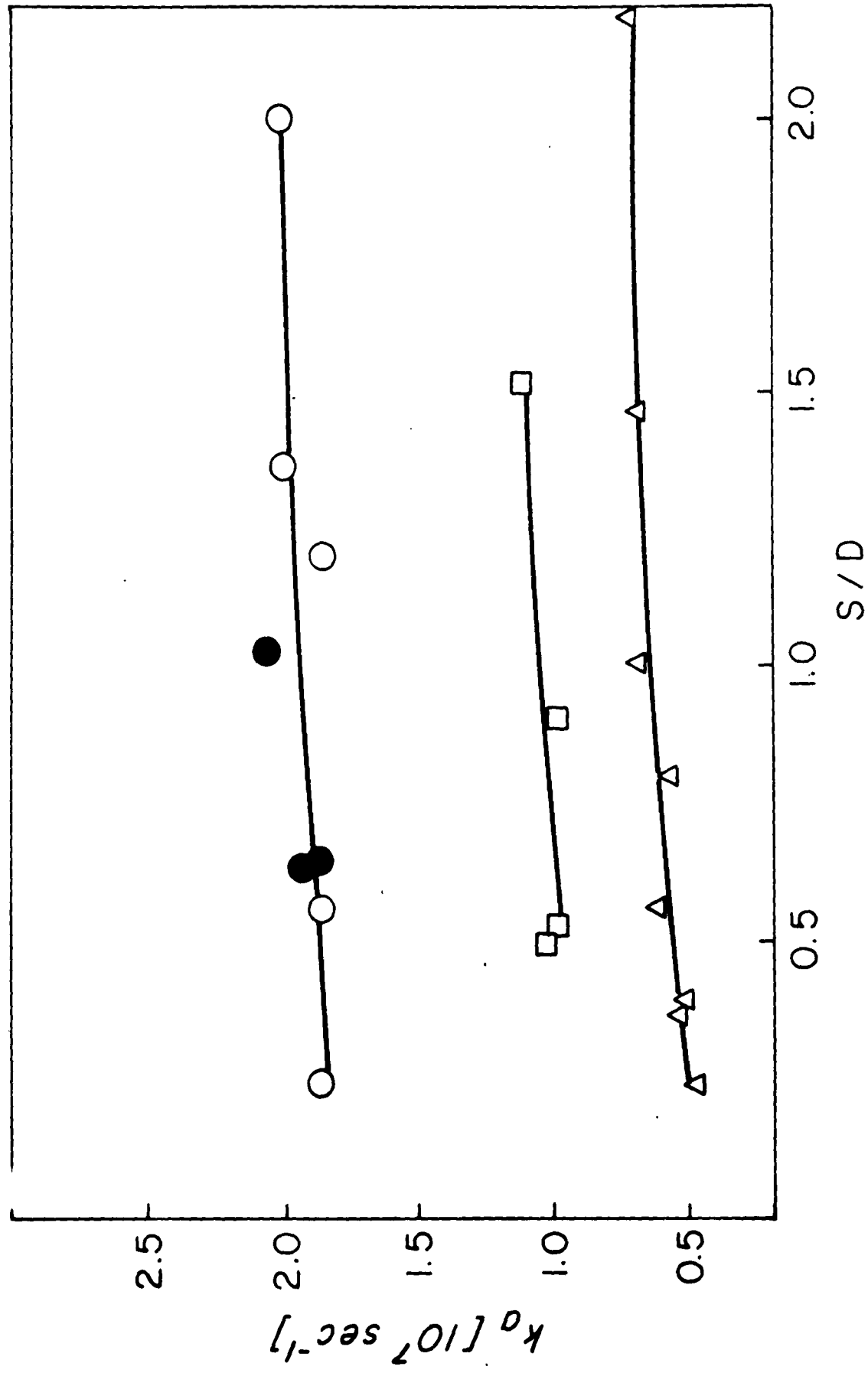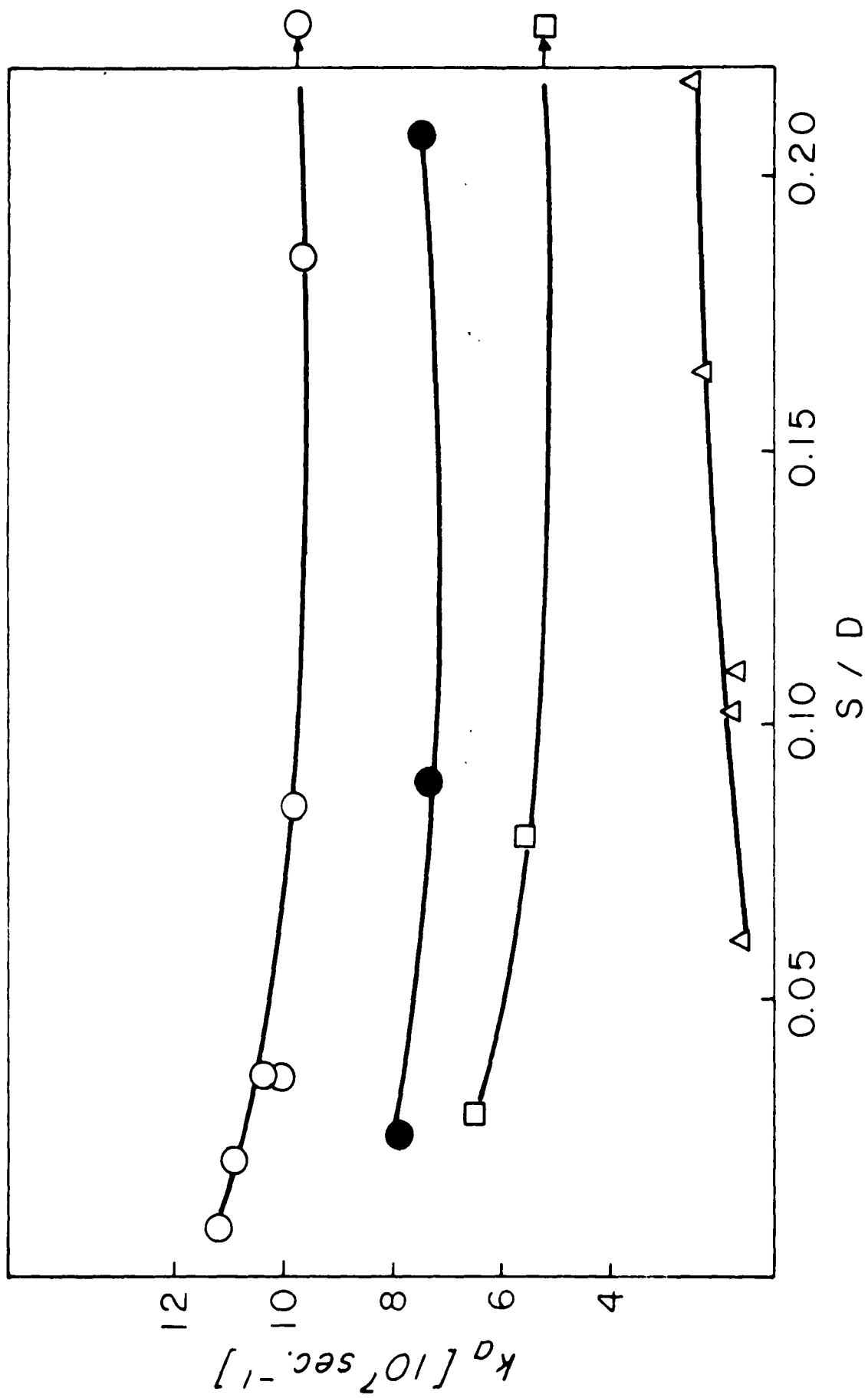
Fig. 1

Fig. 2

k_a $[10^7 \text{ sec}^{-1}]$

S/D

Fig. 3

$k_q \ [10^7 sec.^{-1}]$

S / D

Fig. 4

Fig. 5